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6. AUTHOR(S) J. D. McGERVEY			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) CASE WESTERN RESERVE UNIVERSITY CLEVELAND OH 44106			
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13. ABSTRACT (Maximum 200 words) We have used the positron as a microscopic probe to clarify the connection between the microscopic properties (e.g., free volume distributions) and macroscopic properties (pressure, volume, and temperature relations) of polymers in the glassy state. Measurements of the positron lifetime distribution in the polymer as a function of temperature, aging, and applied strain have shown that positrons are sensitive to the distribution of free volume elements. However, we have also found that refinements in data analysis are necessary, and that we are far from obtaining an unambiguous free-volume distribution from the current results. Theoretical models are being tested to see if they are consistent with the results. We have also generated simulated positron lifetime distributions to test the validity of our curve-fitting methods, and we have discovered that these methods break down when the instrumental resolution curve exceeds approximately 250 nanoseconds in width.			
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FINAL REPORT, ARO CONTRACT NUMBER DAAL03-90-G-0023

MOLECULAR DYNAMICS OF PHYSICAL AGING PROCESSES IN POLYMER GLASSES
(EXPERIMENT AND THEORY)

Case Western Reserve University

John D. McGervey

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STATEMENT OF PROBLEM STUDIED

We have attempted to clarify the connection between microscopic properties (free volume) in polymers and macroscopic properties (relaxation under strain or pressure, overall volume as a function of temperature or pressure, etc.) by using the positron as a microscopic probe. The lifetime distributions of positrons have been measured as a function of temperature, aging, pressure, and applied strain, and the results have been correlated with those of more conventional measurements. In addition, the methods of data analysis have been carefully scrutinized to determine whether some results could be explained as artifacts of the computer fitting program, which is a standard program used in many positron research laboratories.

SUMMARY OF IMPORTANT RESULTS

During this project the most important results were:

- Observation that some polymers are, in a sense, rejuvenated by application of tensile strain. This means that an old polymer, which is no longer shrinking as it ages further, will shrink to a smaller volume after the application and release of tensile strain.
- Confirmation of studies showing that some, but not all, polymers undergo chemical or physical changes as a result of positron irradiation. Thus one must be careful in interpretation of results when using positrons as a probe.
- Simulation of positron annihilation data from polymers, which showed that a simulated curve could not be fitted properly by the most commonly used computer fitting program unless the time resolution function is much narrower than the time resolution that is normally used in polymer studies. This result explains some discrepancies in results that have been reported from different laboratories in studies of polymers of identical composition and history, and it shows what must be done to produce meaningful results.
- Development of apparatus to measure simultaneously the positron lifetime and the total gamma-ray momentum from annihilation of ortho positronium (o-Ps). This apparatus, which needs further refinement, can in principle magnify the o-Ps component in the lifetime spectrum. This is significant, because o-Ps is the probe whose lifetime is affected by free-volume changes in polymers, and it is important to be able to distinguish between o-Ps and other positron states in the positron annihilation results.

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LIST OF PUBLICATIONS

- Positron Annihilation Lifetime Measurements of Free Volume in Polycarbonate Under Tensile Strain*, M. Ruan, H. Moaddel, A. M. Jamieson, R. Simha, and J. D. McGervey, *Bull. Am. Phys. Soc.* 36, 692 (1991)
- Positron Lifetimes and Free Volume in Polycarbonate Under Tensile Strain*, M. Y. Ruan, H. Moaddel, Z. Yu, A. M. Jamieson, R. Simha, and J. D. McGervey, *Materials Science Forum* 105-110 (1992) 1691-1694
- Combined Lifetime-Momentum Measurement of Ortho-Positronium in Polymers*, M. Ruan, W. Zheng, J. D. McGervey, *Materials Science Forum* 105-110 (1992) 1695-1698
- Positron Annihilation Lifetime Studies of Free Volume Changes in Polycarbonate Under Static Tensile Deformation*, M. Ruan, H. Moaddel, A. M. Jamieson, R. Simha, and J. D. McGervey, *Macromolecules* 25, 2407 (1992)
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- Ortho-Positronium Lifetime Studies of Free Volume in Polycarbonates of Different Structures: Influence of Hole Size Distributions*, J.-E. Kluin, Z. Yu, S. Vleeshouwers, J. D. McGervey, A. M. Jamieson, and R. Simha, *Macromolecules*, in press

PARTICIPATING SCIENTIFIC PERSONNEL AND DEGREES AWARDED

Professor J. D. McGervey, Physics Department, CWRU
Professors R. Simha and A. Jamieson, Department of Macromolecular Science, CWRU
Dr. J.-E. Kluin, postdoctoral research associate
M. Franz, (visiting from Germany, 1/92 to 4/92)
P. Hsiang, graduate student (awarded M. S. degree, May, 1990).
H. Moaddel, graduate student (awarded M. S. degree, May, 1991)
M. Y. Ruan, graduate student (awarded Ph. D. degree, May, 1992)
S. Vleeshouwers, graduate student (visiting from the Netherlands, 10/91 to 4/92)
Z. Yu, graduate student (expected to receive Ph. D. in 1994)